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(71)Applicant : NIPPON SYNTHETIC CHEM IND CO
LTD:THE

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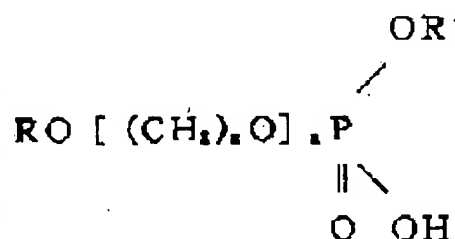
(72)Inventor : SAEKI MASARU

(54) SIZING AGENT COMPOSITION FOR PAPER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a sizing agent composition for paper, excellent in coatability and paper-reinforcing strength and little in adhesivity on the surface of sized paper by compounding a polyvinyl alcohol resin containing carboxyl groups in a specific amount with a specific phosphate ester or its salt.

SOLUTION: This sizing agent composition for paper contains 100 pts.wt. of a polyvinyl alcohol resin having a saponification degree of 10-100%, preferably 50-100%, more preferably 70-100%, and an average polymerization degree of 100-10,000 and containing carboxyl groups in an amount of 0.1-10 mol.%, and a phosphate ester of the formula [R is H, an alkyl or an alkylaryl; (m) and (n) are each an integer; R' is H or an alkoxy] or its salt in an amount of 0.1-50 pts.wt., preferably 0.5-30 pts.wt. The sizing agent composition is coated on a paper substrate so that the carboxyl group-containing polyvinyl alcohol resin is contained in an amount of 0.1-5 g/m², preferably 0.5-3 g/m², as the solid content.



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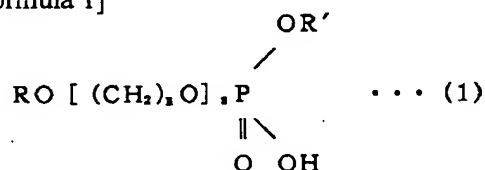
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 CLAIMS

[Claim(s)]

[Claim 1] The sizing agent constituent for papers which contains the phosphoric ester compound shown by the polyvinyl alcohol system resin (A) and the following general formula (1), or its salt (B), and is characterized by the bird clapper.

[Formula 1]



((m and n show hydrogen, an alkyl group, or an alkyl aryl machine.) However, in R, an integer and R' show hydrogen or an alkoxy group.)

[Claim 2] The sizing agent constituent for papers according to claim 1 characterized by a polyvinyl alcohol system resin (A) being a carboxyl group content polyvinyl alcohol system resin.

[Claim 3] The sizing agent constituent for papers according to claim 1 or 2 with which the content of the carboxyl group in a carboxyl group content polyvinyl alcohol system resin is characterized by 0.1-10-mol being %.

[Claim 4] the claims 1-3 to which the content of the phosphoric ester compound general formula [above-mentioned] (1) shown or its salt (B) is characterized by being 0.1 - 50 weight section to the polyvinyl alcohol system (resin A) 100 weight section -- either -- the sizing agent constituent for papers of a publication

[Claim 5] the claims 1-4 characterized by the average degree of polymerization of a polyvinyl alcohol system resin (A) being 100-10000 -- either -- the sizing agent constituent for papers of a publication

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] About the sizing agent constituent for papers, in more detail, it excels in coating nature and this invention relates to the sizing agent constituent for papers with little ***** (adhesiveness) on the front face of paper after processing (sizing).

[0002]

[Description of the Prior Art] Conventionally, a vinyl-ester system resin, especially a polyvinyl alcohol system resin are coated on the surface of paper, in order to improve surface characteristics, such as surface intensity of paper, smoothness, and gloss, and they are widely used as a sizing agent for papers. Paper coated by this sizing agent, Usually, although a calendering roll is passed in order to raise the gloss and smooth nature The paper coated depending on the kind of sizing agent adheres to a calendering roll (setting especially in high humidity atmosphere). A slip of paper etc. arises and it also sets at the time of wet offset printing. by the adhesiveness (*****) of a sizing agent Paper in the place where a sizing agent for papers with small adhesiveness (*****) is desired [in / a damp or wet condition / in the cause by which paper sticks to the blanket cylinder of a printing machine, and the trouble of a slip of paper etc. is caused] As this adhesive (*****) cure, the resin water liquid (JP,53-61705,A) which consists of the polyvinyl chloride system resin powder and water of a water-soluble polyvinyl alcohol system resin and 10 micrometers or less of particle diameters is indicated.

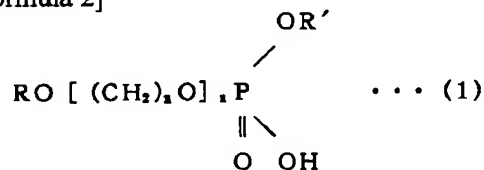
[0003]

[Problem(s) to be Solved by the Invention] However, when the surface paper durability intensity which is the property of an original polyvinyl alcohol system resin is reduced by adding polyvinyl chloride resin powder or **** aqueous liquid becomes waste water, it has a fault, like processing of waste water is difficult, and a sizing agent for papers which can satisfy these faults is desired.

[0004]

[Means for Solving the Problem] Then, this invention person is a polyvinyl alcohol system resin (A), the phosphoric ester compound shown by the following general formula (1), or its salt (B), as a result of repeating research wholeheartedly in view of this situation.

[Formula 2]



(However, in R, m and n show hydrogen, an alkyl group, or an alkyl aryl machine, and an integer and R' show hydrogen or an alkoxy group.) It can excel also in coating nature and the degree of size and paper durability intensity could also be raised, and when a polyvinyl alcohol system resin (A) is a carboxyl group content polyvinyl alcohol system resin, the operation effect of this invention finds out being obtained especially notably, and came to complete this invention.

[0005]

[Embodiments of the Invention] this invention is explained in detail below. Especially the polyvinyl alcohol system resin (A) of this invention is not limited, but can mention the copolymerization saponification object of not only the partial saponification object of polyvinyl acetate but the vinyl ester like the following, and the monomer which may be copolymerized.

The allyl-compound ester stearin acid allyl compound of a saturation carboxylic acid, a lauric-acid allyl compound, a palm-oil-fatty-acid allyl compound, an octylic acid allyl compound, a butanoic acid allyl compound, etc.

Alpha olefin ethylene, a propylene, alpha-hexene, alpha-octene, alpha-decene, alpha-dodecen, alpha-hexa decene, alpha-octadecene, etc.

Alkyl vinyl ether propyl vinyl ether, a butyl vinyl ether, hexyl vinyl ether, octyl vinyl ether, desyl vinyl ether, dodecyl vinyl ether, tetradecyl vinyl ether, hexadecyl vinyl ether, octadecyl vinyl ether, etc.

Alkyl aryl ether propylure RIRUETERU, the butyl allyl-compound ether, the hexyl allyl-compound ether, the octyl allyl-compound ether, the desyl allyl-compound ether, the dodecyl allyl-compound ether, the tetradecyl allyl-compound ether, the hexadecyl allyl-compound ether, the octadecyl allyl-compound ether, etc.

In addition, use of an acrylamide (meta), acrylonitrile (meta), an allyl-compound (meta) sulfonate, an ethylene nature unsaturation sulfonate, styrene, a vinyl chloride, etc. is also possible.

[0006] However, in this invention, although a carboxyl group content polyvinyl alcohol system resin is desirable and this carboxyl group content polyvinyl alcohol system resin is explained in detail below, it is not limited to these. Especially the manufacturing method of a carboxyl group content polyvinyl alcohol system resin is not limited, but can be manufactured by arbitrary methods. For example, although the method of saponifying this copolymer, the method of carrying out the graft polymerization of the monomer which has an oxy-alkylene machine to the polyvinyl alcohol system resin which has ** carboxyl group, etc. are mentioned after obtaining a copolymer from the unsaturation monomer and vinyl-ester system compound which have ** carboxyl group, the method of ** is practical from the manufacture side of a resin, and a performance side. Hereafter, the method of ** is explained concretely.

[0007] As an unsaturation monomer which has a carboxyl group An ethylene nature unsaturation dicarboxylic acid (a maleic acid, a fumaric acid, itaconic acid), or an ethylene nature unsaturated-carboxylic-acid monoester (maleic-acid monoalkyl ester --) Fumaric-acid monoalkyl ester, itaconic-acid monoalkyl ester, or an ethylene nature unsaturation dicarboxylic-acid diester (maleic-acid dialkyl ester --) fumaric-acid dialkyl ester, itaconic-acid dialkyl ester, or an ethylene nature unsaturation carvone acid anhydride (a maleic anhydride --) Monomers, such as itaconic acid anhydride or (meta) an acrylic acid, and these salts are mentioned, and an ethylene nature unsaturated-carboxylic-acid monoester or its salt is used suitably. Moreover, although a formic-acid vinyl, vinyl acetate, a propionic-acid vinyl, a butanoic acid vinyl, a capric-acid vinyl, a lauryl acid vinyl, a BASA tick acid vinyl, a palmitic-acid vinyl, a stearin acid vinyl, etc. can use by independent or combined use as a vinyl-ester system compound, especially vinyl acetate of practicality is high.

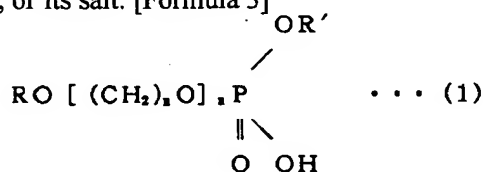
[0008] the **** vinyl ester mentioned above in this invention in addition to the monomer which has a carboxyl group like the above in the case of this polymerization, and the vinyl-ester system compound, and the monomer which may be copolymerized -- less than [50 mol %] -- you make it exist and a polymerization may be performed Although there is especially no limit and a well-known polymerization method is arbitrarily used in copolymerizing, the solution polymerization which usually uses alcohol, such as a methanol or ethanol, as a solvent is carried out. As how to teach a monomer in this method, the whole quantity of a vinyl-ester system compound and a part of aforementioned carboxyl group content unsaturation monomer may be taught first, a polymerization may be started, and arbitrary meanses, such as the method of adding the remaining unsaturation monomer continuously or in division during the polymerization and the method of carrying out package preparation, may be used. A copolymerization reaction is performed using well-known radical polymerization catalyst, such as an azobisisobutyronitril, an acetyl peroxide, a benzoyl peroxide, and a lauroyl peroxide. Moreover, reaction temperature is chosen from the range about 50 degrees C - the boiling point.

[0009] Like the above, next the copolymer which were obtained by carrying out is saponified, and

serves as a carboxyl group content polyvinyl alcohol system resin. In saponification, a copolymer is dissolved in alcohol and it is carried out to the bottom of existence of an alkali catalyst. A methanol, ethanol, a butanol, etc. are mentioned as alcohol. The concentration of the copolymer in alcohol is chosen from 20 - 70% of the weight of the range. It is required to use the alkali catalyst like the hydroxide of alkali metal, such as a sodium hydroxide, a potassium hydroxide, a sodium methylate, a sodium ethylate, and a potassium methylate, or an alcoholate as a saponification catalyst. The amount of this catalyst used needs to make it the 1 - 100 millimole equivalent to a vinyl-ester system compound.

[0010] Although especially a limit does not have saponification temperature in this case, it is desirable to usually choose out of the range of 10-70 degrees C and further 30-50 degrees C. a reaction is usually performed over 2 - 5 hours -- having -- the desirable degree of saponification -- 10-100-mol % -- it is -- especially -- desirable -- 50-100-mol % -- it is chosen from the 70-100-mol range of % especially preferably In addition, when making a vinyl alcohol component contain, it is not restricted to the above-mentioned method, and the method of making oxidation alkenes back-reacting to polyvinyl alcohol (a partial saponification object, full saponification object) for example, etc. can be enforced. Although a carboxyl group content polyvinyl alcohol system resin is obtained in this way, 0.1-10-mol% of the content of this carboxyl group is desirable, and if the content of this carboxyl group has weak paper durability intensity less than [0.1 mol %] and exceeds ten-mol % conversely, it becomes [the solubility when considering as a sizing agent constituent] poor and is not desirable [it is further 0.5-5 mol %, and].

[0011] moreover, this invention -- setting -- the average degree of polymerization of a polyvinyl alcohol (carboxyl group content) system resin (A) -- 100-10000 -- desirable -- further -- it is 300-3000, and if paper durability intensity falls less than by 100, this average degree of polymerization becomes poor [a printability] and 10000 is exceeded conversely, the coating nature or the permeability when considering as a sizing agent constituent fall and are not desirable Next, a phosphoric ester compound or its salt (B) is the compound shown in the following general formula (1), or its salt. [Formula 3]



((m and n show hydrogen, an alkyl group, or an alkyl aryl machine.) However, in R, an integer and R' show hydrogen or an alkoxy group.)

Moreover, the salt of this phosphoric ester compound shows a monoethanolamine salt, ***** sodium salt, potassium salt, a calcium salt, etc. Although it will not be restricted especially if this phosphoric ester compound (B) has the above-mentioned structure, as H.L.B., 5-20 are desirable, and also are 7-16. As the melting point, 50 degrees C or less are 20 more degrees C or less preferably. As the acid number, 40-200 are desirable.

[0012] The sizing agent constituent for papers of this invention is what contains a polyvinyl alcohol system resin (A), the phosphoric ester compound shown by the above-mentioned general formula (1), or its salt (B) like the above (carboxyl group content). Although especially these blending ratio of coal is not limited, the carboxyl group content polyvinyl alcohol system (resin A) 100 weight section is received. It is desirable 0.1 - 50 weight section and also to carry out 0.5-30 weight section content of this phosphoric ester compound or its salt (B). this content under in the 0.1 weight section It becomes [paper durability intensity falls and / a printability] poor and is not desirable, if adhesiveness does not fall but 50 weight sections are exceeded conversely.

[0013] Generally, although the sizing agent constituent for papers of this invention obtained in this way is dissolved and used for water, its solvent system is also usable. What is necessary is just to choose the kind of solvent suitably according to the content rate of the property of a polyvinyl alcohol (carboxyl group content) system resin (A), (A), and (B) etc. For example, comparatively, since the low thing of the degree of saponification is obtained by the shape of a paste, it may use the solvent used for a polymerization or saponification as it is, and as long as it is required, it may

perform solvent substitution. What is necessary is for there to be especially no limit in manufacture of coating liquid, and just to mix the phosphoric ester compound shown in short by water, the above-mentioned polyvinyl alcohol (carboxyl group content) system resin (A), and the above-mentioned general formula (1), or its salt (B). Although what is necessary is just to adjust concentration suitably according to the purpose, especially the concentration of this desirable polyvinyl alcohol system resin (A) is usually chosen from 0.1 - 40 % of the weight, and about further 1 - 20% of the weight of the range in consideration of workability etc.

[0014] Although the sizing agent constituent for papers of this invention contains the phosphoric ester compound shown like the above by the carboxyl group content polyvinyl alcohol system resin (A) and the above-mentioned general formula (1), or its salt (B) The need is accepted. Furthermore, deck-watertight-luminaire-sized agents, such as glyoxal and a urea-resin, a defoaming agent, Well-known additives, such as a release agent, a surfactant, antiseptics, an insecticide, a rust-proofer, and a thickener, can also be added. Moreover, if it becomes in the range which does not spoil the feature of this invention, resins, such as other paper processing agents, for example, other well-known polyvinyl alcohol, starch, a carboxymethyl cellulose, an acrylic latex, and an SBR latex, are also conventionally mixable. Although there is especially no limit as paper which applies the sizing agent constituent for papers of this invention, print sheets, such as the paper boards, such as the Manila ball, a white ball, and a liner, common paper of fine quality, a report grade paper, and a gravure form, a top, inside and lower class paper, a newsprint, etc. are used suitably, for example. In carrying out coating of this sizing agent constituent for papers to this paper, well-known arbitrary methods, such as the size press coating-machine method, the roll-coater method, an EYA Doctor process, the blade coating-machine method, and the SIMM sizer coating-machine method, are adopted.

[0015] A deer is carried out and it is appropriate for the coverage of this sizing agent constituent for papers to make it 0.1 - 5 g/m² (solid-content conversion) and a polyvinyl alcohol (carboxyl group content) system resin (A) become 0.5 - 3 g/m² (same as the above) grade preferably especially. The sizing agent constituent for papers of this invention is applicable to paper by arbitrary methods, such as making Kaminaka mix the so-called internal size method which, of course, dissolves and carries out paper making of the sizing agent constituent for papers of this invention not only the aforementioned method but into pulp distribution liquid, or the sizing agent constituent for papers of a still more powdered and fibrous this invention etc.

[0016] Although the sizing agent constituent for papers of this invention is used as a **** clear coating agent mainly described above, it can use suitably also as a binder for pigment coating, and as a pigment, well-known pigments, such as clay, a calcium carbonate, a kaolin, diatomaceous earth, titanium oxide, an iron oxide, and a satin white, are used. In this binder, the effect which worries do not have the clay shock (phenomenon which a pigment condenses when a binder is added, where a pigment is distributed) which had become a problem in pigment coating conventionally, and was very excellent also about the dispersibility of a pigment is demonstrated.

[0017]

[Example] Hereafter, an example is given and this invention is explained concretely. In addition, among an example, especially, that it is with the "section" and "%" shows weight criteria, as long as there is no notice.

The vinyl acetate 500 section, the maleic-acid 3.4 section, and the methanol 85 section are taught to an example 1 [manufacture of carboxyl group content polyvinyl alcohol system resin (A)] polymerization can. the bottom of churning of the inside of a system, and the inside of a nitrogen air current -- a temperature up -- carrying out -- 60 degrees C -- after the reflux during 30 minutes, and an azobisisobutyronitril -- vinyl acetate -- receiving -- 0.08-mol % -- in addition, the polymerization was performed for 6 hours, the methanol steam after a reaction end was blown, the unreacted monomer was removed, and the methanol solution of a copolymer was obtained Subsequently, the obtained methanol solution was diluted with the methanol to 40%, and it was made 30 degrees C, and neutralized by the sodium hydroxide. Furthermore, the sodium hydroxide was 20 millimole % Added to the vinyl acetate in a copolymer, and it saponified, and the obtained saponification object was filtered, it dried at 70 degrees C, and the carboxyl group content polyvinyl alcohol system resin (degree %, average degree of polymerization 1400 of 99.1 mols of saponification) (A) was obtained. [0018] The (salt B) of phosphoric ester system compound shown in carboxyl group content

polyvinyl alcohol system (resin A) 5.8 above-mentioned section and above-mentioned Table 1 0.2 section is dissolved in the water 94 section. It considered as the sizing agent constituent, and after performing a size press coat (50 m/min, kg [11 / // cm], 6% solution) so that it may become 0.8 g/m² to 60g of basis weights/, and the acid paper of m² by the resin solid content about this constituent, it dried for 2 minutes at 105 degrees C with the cylinder rotating type dryer, it finished in the supercalender further, and sizing paper was obtained. About the obtained sizing paper, evaluation of re-*****, *****, surface paper durability intensity, and the degree of size was performed in the following ways.

[0019] (Re-*****) J.TAPPI According to the splitting strength test method of the No.19"paper board", it did as follows. After being under water for 5 minutes in piles, the felt sides of the obtained sizing paper (100mmx100mm) are inserted into a filter paper, and they are stuck by pressure through a calendering roll by the pressure of 100 kg/cm. Subsequently, adhesive strength (g/30mm) was measured as a test piece with a width of face of 3cm after 24-hour gas conditioning by 20 degrees C and 65%RH with the tension tester ("tensilon UTM-2-20" made from toe yaw BORUDOWIN speed-of-testing:200 mm/min).

(*****) Using the offset rotary press, double-sided printing of one color was continuously performed on sizing paper, and it evaluated as the following.

O --- continuation printing of 10000m or more -- possible ** --- x in which the adhesion in the rotary press (roll) of a sizing agent from 5000m was accepted --- The adhesion in the rotary press (roll) of a sizing agent from 2000m was accepted, and it resulted in ****. [0020] (Surface paper durability intensity) By the IGT printing testing machine (product made from the Kumagai ****), it is FINE to ink. INK IGT pick intensity (cm/second) was measured using TV-20 (Dainippon Ink & Chemicals, Inc. make).

(The degree of size) JIS P Stockigt sizing degree (second) was measured by 8122.

[0021] It evaluated similarly using the salt (B) of the **** (carboxyl group content) polyvinyl alcohol system resin (A) shown in Table 1 according to two to example 6 example 1, and a phosphoric ester compound. In addition, in the example 6, it carried out like the example 1 except having not added a maleic acid at the time of manufacture of a polyvinyl alcohol system resin.

[0022] Except having not added the salt (B) of a phosphoric ester compound in example of comparison 1 example 1, it carried out similarly and evaluated similarly.

In example of comparison 2 example 1, the straight polyvinyl chloride paste resin was used instead of the salt (B) of a phosphoric ester compound, and it carried out similarly, and evaluated similarly. The evaluation result of an example and the example of comparison is shown in Table 2.

[0023]

[Table 1]

Polyvinyl alcohol system resin (A) Phosphoric ester compound (B) Carboxyl group content (mol %)

Content (section) Kind * Content (section) Example 1 0.5 100 ** 3.4 ** 2 1.0 100 ** 6.8 ** 3 0.5

100 ** 3.4 ** 4 1.0 100 ** 6.8 ** 5 1.0 100 ** 3.4 ** 6 0 (native) 100 ** 3.4 Example 1 of

comparison 0.5100 It does not blend but is ** 2. 0.5100 ** 3.4 ***: Set to the above-mentioned general formula (1). Ethanolamine salt [of the phosphoric ester which is R= ethyl group, m= 2, n= 2, and an R'= ethoxy basis] **: Set to the above-mentioned general formula (1), and they are R= methyl group, m= 3, n= 2, and R'= ETOKI. Ammonium-salt **: Set to the above-mentioned general formula (1), and they are R= ethyl group, m= 3, n= 2, and R'= ETOKI. Ammonium-salt **: Straight polyvinyl chloride [0024]

[Table 2]

Re-***** ***** Surface paper durability intensity . The degree of size (g/30mm)

(cm/second) (second) Example 1 3.2 O 270 3.6 ** 2 1.8 O 240 3.8 ** 3 2.6 O 250 3.8 ** 4 1.5 O

240 4.2 ** 5 1.4 O 260 5.5 ** 6 1.6 O 180 Example 1 of 2.8 comparison 5.9 x 280 5.1 ** 2 4.7 x 150 3.9 . [0025]

[Effect of the Invention] Since the sizing agent constituent for papers of this invention contains a polyvinyl alcohol system resin (A) and a specific phosphoric-acid compound, or its salt (B) The adhesiveness (*****) of paper can be prevented, it can excel also in coating nature, the degree of size and paper durability intensity can also be raised, and it can use suitable for print sheets, such as the paper boards, such as the Manila ball, a white ball, and liner paper, common paper of fine

quality, a report grade paper, coat paper (lightweight), a packing form, and a gravure form, a top, inside and lower class paper, a newsprint, etc.

[Translation done.]